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CHEMICAL PROBLEMS IN THE USE OF PROPELLANTS FOR THE SECOND STAGE OF THE EUROPA-1 ROCKET

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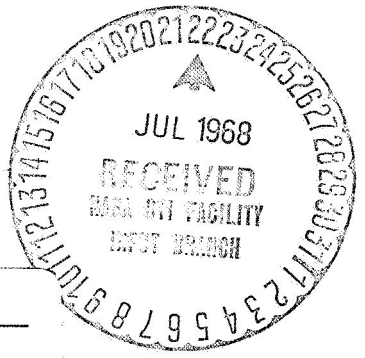

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CHEMICAL PROBLEMS IN THE USE OF PROPELLANTS FOR THE SECOND STAGE OF THE EUROPA-1 ROCKET

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ABSTRACT: After a short account of the synthesis and of the principal properties of the propellants, nitrogen peroxide and unsymmetrical dimethyl hydrazine, the author describes a number of chemical problems concerning specification (analysis) and use (safety precautions and emergency measures).

INTRODUCTION

In 1962 the European Organization for the Development and Construction of /155* Spacecraft Launchers (CECLES) entrusted the responsibility for the second stage of Europa-1 to France. The "rocket" section of the Armaments Division of the Defense Ministry contracted with the Laboratory for Ballistic and Aerodynamic Research of Vernon for the design and construction of the propulsion and piloting system together with overall tests. The second stage uses the propellant combination of unsymmetrical dimethyl hydrazine (dimazine) and nitrogen peroxide. The use of this propellant raised a certain number of chemical problems whose solutions are derived either from American technology (specifically for the fuel) or are largely original (in regard to the oxidizer). For the sake of clarity, the /156 two components will be treated separately. However, it should be noted that this combination is a "hyperpropellant" ["hypergolique"] and has an ignition delay of 4 to 5 milliseconds as measured with the method of [1] under ambient conditions on the ground.

UNSYMMETRICAL DIMETHYL HYDRAZINE

General Remarks

Dimazine, $(CH_3)^2N\text{-}NH_2$ is presently being manufactured in the United States by Food Machinery Chemical Company (dimazine) and by Olin Mathieson Chemical Company (UDMH). It is manufactured by reaction of a dimethylamine salt with sodium nitrite and subsequent reduction of the product as shown below:

$$(CH_3)^2\,NH + NOOH \rightarrow (CH_3)^2\,N\text{—}NO + H_2O$$
$$(CH_3)^2\,N\text{—}NO + {}_2H^2 \rightarrow (CH_3)^2\,N\text{—}NH^2 + H^2O.$$

This is a liquid product with a wide range of temperature (boiling point 63 °C,

*Numbers in the margin indicate pagination in the foreign text.

melting point -57 °C), density 0.785 at 25 °C, colorless or slightly yellow and clear with the smell of ammonia. It is highly hygroscopic, oxidizes in the air (must be stored under nitrogen pressure), and reacts with carbon dioxide. The vapors are toxic (maximum permissible concentration 0.5 to 5.0 ppm in the literature), very inflammable (flash point + 1 or - 15 °C depending on method of measurement), and explosive concentrations in the air range from 2 to 99%.

Safety Problems

Accidental contact with the skin is not serious. Since the product is caustic, the affected parts should be thoroughly washed with water. Protection against vapors is provided by gas masks of the ammonia type for personnel handling small quantities of the liquid (laboratories). A regular gas mask is required for personnel handling large quantities (storage points) who must also wear protective clothing when handling the liquid. If any of it is spilled, it must be diluted by a large amount of water and drained toward a water treatment station. /157

Accidental escape of vapors has never occurred. However, in decompressing containers and tanks, there is always present vapor which must be trapped. Such vapor must be passed through a chemical trap of pumice stone saturated with a solution of hydrochloric acid. After service, the trap must be washed with a large amount of water and the strongly diluted solution drained toward the treatment station [17]. If the fuel becomes contaminated under certain conditions, it is stored and then destroyed, by combustion with nitrogen peroxide, in a remote area with all necessary safety measures.

Quantitative analysis of the substance in air can be made by an American method of colorimetry utilizing sodium aminoprussiate which turns red and the amount of admixture is measured optically by monochromatic light with a wavelength of 490 mμ [3].

Problems of Analytical Chemistry

A) Acceptance analysis of the fuel: the specifications [4] are directly derived from and very close to the American standard [5]. Determination of volume is made with the Lipkin pycnometer [6]; optical transmission at 440 millimicron is measured in 50-mm cells in relation to distilled water [7]; the distillation curve is plotted with a standard method [8]; water content is determined by absorption spectrometer at 1.94 micron [9] and potentiometric titration through potassium iodate in a concentrated hydrochloric medium when cold [10] from the reaction:

$$IO_3K + 2\,ClH + 2\,(CH_3)^2N{-}NH^2 \rightarrow 3\,H_2O + ClK + ClI + (CH_3)^2N{-}N{=}N{-}N(CH_3)^2.$$

The principal difference between French and American specifications lie in the last two points. Titration with potassium iodate is made in the LRBA [Vernon Laboratory] after obtaining samples in sealed tubes under nitrogen pressure and

hydrochloric dissolution is also made under nitrogen pressure which prevents errors of measurement. Water content by distillation as in the American specifications was examined and has not been retained for acceptance analysis [11]. Measurement of melting point [12] has also not been retained. /158

B) Complete analysis of the fuel: complete qualitative analysis of dimazine is made by chromatography in the gaseous phase [13]. The polarity of the constituents made it necessary to utilize a 35-60 mesh teflon as support where the stationary phase is a mixture of 2% of tetrahydroxyethylethylenediamine (THEED) and 2% of carbowax 400. Analysis is made with hydrogen as carrier gas (volume 46 cm^3/min) at 80 °C. The components are eluted in the following order: ammonia, NH_3; dimethylamine, $(CH_3)_2NH$; methylene dimethyl hydrazine, $CH_2=N-(CH_3)^2$; dimethyl hydrazine, $(CH_3)^2N-NH_2$; water, H_2O; nitrosodimethylamine, $(CH_3)^2-N-NO$.

Determination of water content by chromatography in the gaseous phase is presently being investigated. In regard to this, [14] and [15] are of particular interest. Preparation of sufficiently efficient chromatographic columns by using powdered teflon as support presents a certain number of difficulties due to phenomena of electrostatics and agglomeration after deposition of the stationary phase.

NITROGEN PEROXIDE

General Remarks

Nitrogen peroxide, NO_2 or N_2O_4, is produced in France only as an intermediate product in the preparation of nitric acid. Consequently, there are no plants producing nitrogen peroxide but only nitric acid in France so that nitrogen peroxide is obtained during this process. Only synthetic preparation of nitric acid is suitable for separation of nitrogen peroxide. The most widely distributed method of synthesis in France uses oxidation (by air or oxygen of ammonia on platinum gauze.

$$_2NH_3 + \frac{5}{2} O^2 \rightarrow 3\ H_2O + {}_2NO$$ /159

The gases are then cooled and the water from combustion condensed. Additional air oxidizes nitrogen oxide to nitrogen peroxide (NO_2 and N_2O_4) in large-capacity towers under 3 to 7 bar in accordance with the process

$$NO + \frac{1}{2} O \rightarrow NO_2$$

It is also possible to dissolve the peroxide from the oxidation towers in diluted nitric acid and subsequently oxidize it with ozygen at 50 bar in the autoclave. This furnishes a concentrated red nitric acid from which the nitrogen peroxide is separated by distillation and fractional condensation (Bamag-Hoko process). Nitrogen peroxide remains liquid within a normal range of temperature (boiling point + 21 °C, melting point — 11.2 °C), has a density of 1.458 at 15 °C, and its smell is sweetish or acid as a function of concentration. Nitrogen peroxide in the liquid state exists in a single molecular form but maintains an equilibrium between monomeric NO_2 and dimeric N_2O_4

$$N_2O_4 \rightleftharpoons 2\,NO_2\,.$$

This equilibrium is displaced to the right when the temperature rises. This changes the color of the substance with temperature. N_2O_4 is colorless and NO_2 is red. In the solid state it is colorless whereas the gaseous phase is yellow around — 10 °C. When the temperature rises, it turns red and then brown. A layer 2 cm thick is almost black at 150 °C. Beyond this temperature, the color becomes lighter due to dissociation

$$2\,NO_2 \rightleftharpoons 2\,NO + O^2.$$

Vapor tension reaches about 2.3 bar at 40 °C. The vapors are toxic (maximum permissible concentration 5 ppm under exposure for 8 hours per day and 5 days per week).

Destruction of Accidental Spills and Escapes

Due to the low boiling point of nitrogen peroxide, the emergency crew always encounters 2 problems: (a) control of the highly mobile vapor phase; (b) control of the liquid phase constantly turning into the vapor phase.

We must not lose sight of the fact that nitrogen peroxide is a rapidly lethal gas in high concentrations (e.g. generally pulmonary edema) and that its vapors are heavier than air ($d_{air} = 2.8$) and therefore remain close to the ground with insufficient movement of the air and when thermal equilibrium exists. In order to solve these problems, it was necessary to develop methods of chemical control for each of the 2 phases. /160

1. Control of the Vapor Phase

We first turned to water or solutions of chemical reagents in powder form. Neither of these methods was sufficiently effective because the reactive surface between the substance is always too small. The ideal would have been to prepare an aerosol of the destructive reagent. In order to increase the surface of reaction, we turned to gaseous reagents which had the advantage of following the

movement of the peroxide vapor in the air. Industrially available are two gases, hydrogen sulphide and ammonia, which react strongly with nitrogen peroxide.

Hydrogen sulphide (H_2S) has a rotten egg smell and is toxic. The maximum permissible concentration is 20 ppm (4 times less than N_2O_4). It has the further disadvantage of producing explosive mixtures in air within a range of concentration of 4.3 to 46.0%-vol. It is also heavier than air ($d_{air} = 1.18$) and any excess volume of the reagent sinks to the ground. It was eliminated from consideration for these 3 reasons and no tests were made.

Ammonia (NH_3) is produced on a large scale in France. It has a suffocating smell and maximum permissible concentration of 100 ppm (20 times less than N_2O_4). It produces explosive mixtures in air within a range of concentration of 17 to 27%-vol or considerably narrower than hydrogen sulphide. It is both lighter than air ($d_{air} = 0.59$) so that it is automatically dispersed if the safety zone is sufficiently large, and is also very soluble in water and can therefore be neutralized with spraying by water when necessary.

Tests for destruction of nitrogen-peroxide vapors were started with 5 kg and concluded with 600 kg of the substance. The reaction in the gaseous phase is instantaneous and the cloud becomes white through formation of ammonium nitrate from the reaction

$$2\,NO_2 + 2\,NH_3 \rightarrow NO_3\,NH_4 + N_2 + H_2O.$$

The reaction does not create any toxic product but there is the risk of formation of ammonium nitrite which is toxic. Analysis of the reaction products indicated the formation of 18 ppm so that, in order to absorb as much nitrite as is contained in a single tablet of some medications, it would be necessary to absorb about 6 kg of the solid reaction product. Moreover, ammonia is lighter than air and tends to carry nitrogen peroxide upward. It should also be noted that the reaction takes place under great reduction of volume and limits the spread of the cloud. /161

Employment of this process makes it necessary to provide for the absence of an open flame due to the risk of explosion. Accordingly, the control equipment must be mobile and must be located at a certain distance from engine or rocket test stands. Its use in fog is questionable due to the possible formation of an ammonia aerosol. However, in spite of these inconveniences, ammonia is still the best means available to control nitrogen-peroxide vapors.

2. Control of the Liquid Phase

It is obvious that control of the liquid phase is no less important than that of the vapor phase since the liquid phase will always produce a vapor phase under exposure to air. Consequently, there is required a means of destruction or at least of "blocking" of liquid nitrogen peroxide and tests in this direction have been

carried out [16]. From the chemical viewpoint, the principal functions of nitrogen peroxide are: (a) its oxidoreduction capability; (b) its character as anhydrous acid. These functions have been utilized in the attempted chemical destruction of nitrogen peroxide.

It should be noted, however, that the method of destruction based on the oxidizing character of nitrogen peroxide is effective only if it involves chemical reactions converting peroxide into a nitrous compound. There exist numerous oxidizing reactions by N_2O_4 which lead to the formation of nitrogen oxides lower than N_2O_4 and specifically nitric oxide (NO). The latter reoxidizes spontaneously at ambient temperature through simple contact with the oxygen of the air and thus reforms nitrogen peroxide. Among the oxidation reductions through N_2O_4, there /162
are those with ammonium nitrate (NO_3NH_4) ammonium sulphate ($SO_4(NH_4)^2$), and urea ($CO(NH_2)^2$) in accordance with the equations:

$$NO_3NH_4 + 2\,NO_2 \rightarrow N^2 + 2\,NO_3H + H_2O$$
$$SO_4(NH_4)^2 + 4\,NO_2 \rightarrow 2\,N^2 + 2\,NO_3H + SO_4H_2 + 2\,H_2O$$
$$CO(NH_2)^2 + 2\,N_2O_4 \rightarrow 2\,NO_3H + CO_2 + 2\,N^2 + H_2O$$

Most of these reactions are too slow and occasionally form foam which increases the duration of contact with the reagents. We have attempted to further increase the duration of contact by the addition of surface-active agents promoting the formation of foam without obtaining very convincing results. All these reactions are of interest but do not take place except in the presence of water. Unfortunately, it is not possible to go too far along this path because the reaction of water and nitrogen peroxide is exothermal and results in considerable vaporization of the substance which accelerates the formation of the gaseous phase. Among the reactions based on the character of anhydrous acid of nitrogen peroxide, we investigated the reactions with calcium oxide, calcium carbonate and sodium hydroxide.

Unfortunately all these reactions are highly exothermal since they take place easily and rapidly bring liquid peroxide to the boiling point. Moreover although some of these reactions are ideal from the strictly chemical point of view, e.g. the reaction with caustic soda:

$$2\,NaOH + N_2O_4 \rightarrow NO_3Na + NO_2Na + H_2O,$$

others are less so due to assumed secondary reactions:

$$2\,CaO + 2\,N_2O_4 \rightarrow (NO_3)^2\,Ca + (NO_2)^2\,Ca$$
$$(NO_2)^2\,Ca + N_2O_4 \rightarrow (NO_3)^2Ca + 2\,NO$$
$$2\,NO + O^2 \rightarrow N_2O_4$$

so that it appears impossible to fix all of the nitrogen of the peroxide in the form of salts without excessive consumption of calcium. Tests in this direction therefore were unsuccessful and also by reason of the rapid rise of temperature. It was therefore necessary to find a reaction taking place easily and without major exothermal effect, but the two conditions are somewhat contradictory.

We therefore investigated products somewhat analogous to complex compounds, specifically through reaction of nitrogen peroxide with zinc or zinc oxide in powder form /163

$$Zn + 4\,N_2O_4 \rightarrow Zn(NO_3)^2,\ 2\,N_2O_4 + 2\,NO.$$

Unfortunately these reactions do not take place readily enough to be used as means of control.

We then investigated precipitation reactions of which there are not many since all common nitrates and all nitrites are soluble. However, it is possible to turn to the formation of a solid compound of anhydrous acid. There are also not very many of these compounds but we found one offering the possibility of blocking nitrogenperoxide. Through simple addition, commerical perchloric acid (65-70% acid) with nitrogen peroxide instantly gives a white and heavy curdled precipitate where the liquid phase passes through several greenish-blue tints due to the reaction of the peroxide with the water of the perchloric acid solution with the liberation of peroxide. Liberation can be rapidly stopped by using a slight excess of perchloric acid. Tests have shown that this reaction, not yet reported in the literature, must be

$$ClO_4H + N_2O_4 \rightarrow ClO_4NO + NO_3H$$

in which the exothermal effect is very slight and the vapor losses low.

This affords a means of control of liquid nitrogen peroxide (and even gaseous in some special cases). However, the method should not be considered as a destruction process but rather as a "blocking" process so that the acid products must subsequently be destroyed. However, it is noteworthy that the control crew was able to arrest continued formation of the gaseous phase by blocking the peroxide. This makes it possible to carry out destruction later which would not have been possible without previous blocking. Final destruction is made by hydrolysis in an oxidizing medium followed by fixation through a base.

Destruction of Spills and Escapes Under Normal Conditions

Under normal conditions vapors are only formed during decompression of the containers or tank trucks supplying the tanks at storage points. Control of such vapors is much easier than under accidental release of a cloud of nitrogen peroxide. The volume to be destroyed is known approximately at any given moment and given location and, when necessary, decompression can be made /164

gradually and controlled as desired. It appears that such destruction is carried out in the US by conducting the vapors into the base of a plate tower in which it passes through a descending flow of caustic-soda solution which is recirculated by pumping.

We turned to a different solution which consists in conducting the noxious vapors into the bottom of a cylindrical tank filled with pumice stone moistened by a saturated solution of urea when the tank is in use. The reaction is exothermal and vaporizes a part of the water which limits the rise of temperature in the zone of reaction. No toxic product results from this process

$$N_2O_4 + CO(NH_2)^2 \rightarrow NO_3NH_4 + CO_2 + N^2$$
$$N_2O_4 + NO_3NH_4 \rightarrow N^2 + 2\,NO_3H + H_2O.$$

After use, the pumice stone is washed with running water, dried and recharged with urea [17].

Control of the nitrogen-peroxide content of the air is easily made by colorimetry of the nitrites resulting from the alkaline dissolution of the peroxide. The nitrite reacts with the sulphanilic acid in a hydrochloric medium and subsequent combination with naphthylamine forms a red dye. Measurement is made by optical absorption at 520 mμ which permits determination of nitrogen peroxide to within 1 ppm [18].

Analysis of Nitrogen Peroxide

Analysis of industrial nitrogen peroxide raised and still raises a certain number of analytical problems which are difficult to solve both by reason of the extent of nitrogen chemistry and of the many equilibria in the chemistry of nitrogen oxides. We should remember here that the investigation was made with nitrogen peroxide manufactured by the Bamag-Hoko process.

Qualitative analysis was made by mass spectrometry at the Central Explosives Laboratory and indicated that the product must be either a binary compound (N_2O_4-NO_3H) or a ternary compound (N_2O_4-NO_3H-H_2O). The product is consequently different from the American product defined in US Airforce Standards [19].

Quantitative analysis [20] of our product which is assumed to be no more /165
than ternary, therefore formulation of three equations. Before giving these equations, we shall briefly review the reactions of water with nitrogen peroxide. It is assumed that the first step is the formation of a mixture of nitric and nitrous acid as a function of equilibrium

$$N_2O_4 + H_2O \rightleftharpoons NO_3H + NO_2H$$

and that this equilibrium is followed by an internal oxidoreduction of the nitrous acid

$$3\,NO_2H \rightleftharpoons NO_3H + 2\,NO + H_2O.$$

The overall reaction in an aqueous medium therefore is

$$3\,N_2O_4 + 2\,H_2O \rightleftharpoons 4\,NO_3H + 2\,NO$$

which is more generally written in the form

$$2\,N_2O_4 + H_2O \rightleftharpoons 2\,NO_3H + N_2O_3$$

and is equivalent due to the high dissociation of the nitrous anhydride

$$N_2O_3 \rightleftharpoons NO_2 + NO.$$

The molecule of nitrogen peroxide possesses 1 x N^{5+} (pentavalent = nitric) and 1 x N^{3+} (trivalent = nitrous). Hydrolysis (a) forms an equimolecular mixture of nitric and of nitrous acid but, as a function of the reaction (b) due to the instability of the nitrous acid, a part of the nitrous nitrogen N^{3+} converts to nitric nitrogen N^{5+} and the other part converts to N^{2+}. These secondary reactions do produce themselves in mixtures of N^{5+} and N^{3+} since they occur with samples of liquid peroxides in aqueous solutions of reagents. In fact, if the test tube containing the sample breaks in the reactive aqueous medium, this always produces locally and for a brief time an excess of nitrogen peroxide in relation to the reagent and the peroxide then reacts with water in accordance with equations (a) and (b). We shall see further below the importance of these secondary reactions.

For analysis in accordance with the Specifications [21], the 3 equations are furnished:

1. through reaction of nitrogen peroxide with an excess of soda in the presence of air or oxygen and by subsequently determining the excess of soda "by return" to sulphuric acid until color change ["virage"] of phenolphthalein. This makes it possible to determine total nitrogen N_t in % which is the sum of (a) the nitrogen of nitric acid, $N^{5+}_{NO_3H}$ in %; (b) the pentavalent nitrogen of N_2O_4, $N^{5+}_{N_2O_4}$ in %; (c) the trivalent nitrogen of N_2O_4, $N^{3+}_{N_2O_4}$ in %. Determination must be made in the presence of air in order to avoid the loss of nitric oxide formed during the reaction (b). The nitric oxide is not soluble in soda. In order to adsorb it /166

by the latter, the nitric oxide must be re-oxidized with nitrogen dioxide

$$NO + O \rightarrow NO_2$$

which is easily transformed into nitrite and nitrate from the equation

$$2\,NO_2 + 2\,NaOH \rightarrow NO_3Na + NO_2Na + H_2O.$$

This results in total fixation of the nitrogen of the peroxide and the determination of total nitrogen is accurate. However, it is not possible to utilize an aliquot sample for determination, e.g., of nitrite because the distribution of N^{5+} and N^{3+} after dissolution in the soda is no longer representative of the distribution of the 2 forms in the product due to the presence of reaction (b).

2. through reaction of the nitrogen peroxide with an excess of cerium sulphate in a sulphur solution under nitrogen pressure. The excess of cerium sulphate is subsequently determined "by return" to ferrous ammonium sulphate and utilizing orthophenanthroline (or 1, 10-phenanthroline or "ferroine") as indicator of color change. The [electric] potential of turning color change of this indicator in a sulphuric medium is 1.10 V and therefore agrees well with that of the cerium salts (E_o = 1.45 V). We were able to verify satisfactory agreement between visual and potentiometric color change. This makes it possible to determine trivalent nitrogen, N^{3+}, in % which originates from the trivalent nitrogen of N_2O_4, $N^{3+}_{N_2O_4}$ %. This determination is quantitatively exact, i.e. the result does represent the percentage of trivalent nitrogen of N_2O_4 but actually and always due to the secondary reaction (b), the NO formed in this reaction also reacts. However, this does not influence the determination both because this secondary reaction is an internal oxidoreduction and therefore has a constant electronic equilibrium ["bilan"]

$$3\,NO_2H \rightleftharpoons NO_3H + 2\,NO + H_2O$$

or /167

$$3\,N^{3+} \rightleftharpoons N^{5+} + 2\,N^{2+}$$

and also because the oxidation potentials of N^{3+} and N^{2+} in N^{5+} are closely adjacent and lower than those of the cerium salts (E_o = 1.45 V). However, it is absolutely necessary to take such measurements under nitrogen pressure

$$N^{2+} \rightleftharpoons N^{3+} + e \qquad (E_0 = 0{,}99\ V)$$
$$N^{3+} \rightleftharpoons N^{5+} + 2e \qquad (E_0 = 0{,}94\ V)$$

3. any water present is calculated from the difference to 100 where the 3rd equation is based on the qualitative analysis through mass spectrometry. The calculations are based on the fact that:

$N^{3+}_{N_2O_4}\ \% = N^{5+}_{N_2O_4}\ \% = N^{3+}\ \%$ determined by measurement of cerium.

From this we obtain N_2O_4 in % and

$$N^t\ \% - 2\,N^{3+}_{N_2O_4}\ \% = N^{5+}_{NO_3H}\ \%$$

allows us to calculate NO_3H in %. Any water present is calculated from the difference to 100.

Let us briefly note here that determination by oxidation (with cerium sulphate) had previously been investigated with potassium permanganate (E_o = 1.5 V) but this reagent was eliminated due to abnormal wine-red coloration during color change and also by reason of a lack of flexibility in the amounts of excess reagent. It should also be pointed out that it was necessary for us to develop a simple device to fill the sampling tubes [22]. Although nitrosyl chloride (NOCl) is not present in our product (it does exist in the American product), we also investigated a method of determination of this compound in case it should become necessary to buy nitrogen peroxide in the US. This is a determination with silver chloride after destruction of the nitrides by amidosulphuric acid. As far as we know, this is an original method which was shown to be very accurate and sensitive if a recording instrument for potentiometric titration is available.

Reaction of Nitrogen Peroxide Under Storage

Experience has shown that nitrogen peroxide is virtually free of water on delivery. Successive analyses indicate that N_t % remains constant in storage. /168
In prolonged storage, N^{3+} % and the product becomes less of a reducent because it necessarily oxidizes. Assuming qualitative analysis to be accurate, we may assume that this oxidation is due to the reaction

$$N_2O_4 + \frac{1}{2}O^2 \rightarrow N_2O_5$$

if N_2O_4 has 1 N^{5+} and 1 N^{3+} per molecule. N_2O_5 has 2 N^{5+} per molecue but this reaction does not seem very probable because it requires ozone [24]. This might possibly take place in the presence of free water from the reaction

$$N_2O_4 + \frac{1}{2}O^2 + H_2O \rightarrow 2\,NO_3H$$

but, as pointed out precedingly, the nitrogen peroxide does not contain any significant amount of water on delivery.

For a valid explanation of this behavior, it is possible to assume — but presently without direct proof — that the industrial product contains other nitrified types of molecules with a rate of oxidation lower than that of the nitrogen of N_2O_4. One or several of these products may not have shown up during qualitative analysis for unknown reasons. Such possible products may be N_2O_3 (or NO_2H) which oxidize easily. It may well be assumed that the chain of transformation

$$NH_3 \rightarrow NO \rightarrow N_2O_3 \rightarrow N_2O_4$$

is not complete during industrial manufacture and that there may remain a nitrogen oxide lower than N_2O_4 from the point of view of rate of oxidation which can apparently only be NO or N_2O_3 which is the same due to the equilibrium

$$N_2O_3 \rightleftharpoons NO_2 + NO.$$

The product would than be a quaternary mixture with the following equilibrium

$$2\,N_2O_4 + H_2O \rightleftharpoons 2\,NO_3H + N_2O_3$$

In order to carry out analysis, it would than be necessary to add a 4th equation to the 3 already given and to define the physical conditions which will destroy this equilibrium. However, this equation cannot be found only through chemistry so that the methods of physics will be needed to solve this problem.

If we apply the method of analysis given in the Specifications to this quaternary mixture, the following should be noted: (1) the determination of total nitrogen remains exact; (2) the determination of trivalent nitrogen remains exact; (3) calculation of water content can no longer be made and any interpretation of the result of the preceding determinations is incorrect. Actually, the Specifications are based on the hypothesis that the only compound containing trivalent nitrogen is N_2O_4 which contains one per molecue but, if N_2O_3 is present, this is no longer /169

true since the products of hydrolysis of this compound react on cerium sulphate with trivalent nitrogen. By carrying out calculation with N_2O_4, we find that 1 % of N_2O_3 is interpreted as 2.4% of N_2O_4 which falsifies the result.

Method Under Investigation

This method under investigation has two objectives: (1) development of a method making it possible to evade the problem; (2) development of a method making it possible to solve the problem. The problem of analysis posed by the equation

$$2\,N_2O_4 + H_2O \rightleftharpoons 2\,NO_3H + N_2O_3$$

is insoluble in the present stage of our knowledge but the problem may be evaded by presenting the equation in a different manner: actually

$$2\,N_2O_4 = N_2O_5,\ N_2O_3$$

and

$$2\,NO_3H = N_2O_5,\ H_2O$$

are conventional formulations which correspond to chemical reality. The equation to be investigated can then be written

$$N_2O_5,\ N_2O_3 + H_2O \rightleftharpoons N_2O_5,\ H_2O + N_2O_3$$

and the compound can be considered to be ternary. Cerimetric determination always gives the result

$$N^{3+}\ \% = N^{3+}_{N_2O_4}\ \% + N^{3+}_{N_2O_3}\ \%$$

so that we then calculate for total anhydrous nitrogen, $N_2O_3^t$ %, but are not able to give the distribution of true N_2O_3 and ficticious N_2O_3 combined in the form of N_2O_4.

Total nitrogen determination remains exact and furnishes /170

$$N^t\ \% = N^{5+}_{NO_3H}\ \% + N^{5+}_{N_2O_4}\ \% + N^{3+}_{N_2O_4}\ \% + N^{3+}_{N_2O_3}\ \%.$$

From the difference between N_t% and N_3^t%, we obtain the total pentavalent nitrogen

$$N^t\,\% - N^{3+}\,\% = N^{5+}_{NO_3H}\,\% + N^{5+}_{N_2O_4}\,\%$$

which can than be calculated as total anhydrous nitrogen, $N_2O_5^t$%, without being able to give the distribution of N_2O_5 combined in the form of nitric acid or combined in the form of nitrogen peroxide. Total water, H_2O_t%, is then calculated from the difference to 100 without being able to give the distribution between free water and combined water. The results are ultimately plotted in a ternary diagram of $N_2O_3^t$%, $N_2O_5^t$%, H_2O^t%.

This method has the considerable advantage to require no hypothesis and is exact even in the presence of additional nitrous acid, NO_2H which reacts as 1/2 (N_2O_3, H_2O). The method gives a total breakdown of the product without entirely solving the problem.

In an attempt to solve the problem, our efforts are presently oriented toward selective determination of the nitric acid. For this purpose, we have adopted the methods of physics or combined physical and chemical methods.

In the near infrared, nitric acid has a characteristic absorption band (1.47 μ). Tests have shown that the absorption band can be used for determining NO_3H but we still need to ascertain, if nitrous acid (NO_2H) is present, whether this compound has an absorption band in this region of the spectrum. In order to do so, it is evidently necessary to have available as reference a nitrogen peroxide not containing nitric acid so that it was necessary to investigate a method of purification of this substance [25]. It is also necessary to have quartz cells, in the section covered by the optic beam, fused to pyrex so that they can be easily sealed after filling. It will also be necessary to provide a thermostatic device for the cells.

The 2nd proposed method has already been used by Sanfourche and is based on the difference of vapor tension of the components present in millimeters of mercury as shown below: /171

	à 0°C	à 10 °C
N_2O_3	608	> 760
N_2O_4	176	453
NO_3H	14.2	26.5
H_2O	4.6	9.2

The principle consists in passing a stream of anhydrous nitrogen through the thermostat-controlled sample in such manner as to entrain all of the N_2O_3 and

the greater part of N_2O_4. We then have a red nitric acid which can be analyzed with the method of the Specifications.

If the test is carried out at 0 °C as indicated by Sanfourche, it seems that the percentage of nitric acid found is systematically lower than the percentage introduced, by reason of "vesicular entrainment" or by reason of the partial vapor tension of NO_3H and of the large volume of nitrogen used for "bubbling" [barbotage]. By contrast, the results obtained at 10 °C presently appear more valid. The difficulty resides in detecting the moment when bubbling must be arrested.

Also proposed by Sanfourche, the 3rd method for determination of NO_3H and investigated by Allied Chemical Company for determination of "equivalent" water, utilizes both the difference of vapor tension and the phenomenon of phase separation which is manifested when the concentration of nitric acid in the peroxide reaches maximum solubility. According to [26], the solubility of nitric acid in nitrogen peroxide is 4.7%. From the values given by [27] and extrapolated to 0 °C, it is 4.1%. According to [28], it is 4.6%.

The volume of the sample is measured at 0 °C. The nitric acid is then concentrated by entraining the components with higher vapor tension in anhydrous nitrogen. When the concentration of nitric acid reaches maximum solubility at the respective temperature, there appears a 2nd more concentrated acid phase in the form of cloudiness in the mass. The nitrogen stream is then cut off and the volume of the residue measured. The percentage of nitric acid can then be obtained through simple calculation.

Tests of the method are under way which appears very reproducible but its accuracy needs to be further verified by analysis of mixtures of known content and determination of the coefficient of solubility to be adopted.

Outside of all these efforts basically oriented toward quantitative analysis, a qualitative investigation based on absorption spectrometry in the infrared (1-15 μ) is under way in the Infrared Laboratory of the Central Armament Laboratory which designed and constructed a special cell making it possible to record infrared spectra in the liquid phase. /172

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